

CHEMISTRY OF THE INORGANIC AZIDES

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1. Introductory Survey

THE first azide to be prepared was phenyl azide, which was made by Griess in 1864; Curtius in 1890 obtained sodium azide and from it aqueous hydrazoic acid. Both organic and inorganic azides have always been thought remarkable, particularly for their unusual structure, their instability, and their wide range of reactivity. The inorganic azides have been the subject of two extensive reviews, the earlier¹ dealing mainly with their chemistry and the later² with their physical properties.

In this Review, inorganic azides, and especially solid ionic azides, receive most attention. The arrangement which has been chosen attempts to set them in perspective, and includes outline accounts of hydrogen azide and the simplest organic azides. Systems of successively increasing complexity are presented; the molecular azides are here followed by the isolated azide ion before the ideal ionic-crystalline lattice is reached. Into this scheme, the azide radical $\cdot\text{N}_3$ is also fitted. Its key position (the "positive hole" in the terminology of the defect ionic lattice) in the decompositions of solid azides calls for its closer examination, and its occurrence in the gaseous, aqueous, and glassy states adds to its interest. This is the order of arrangement adopted in discussion of both structure and thermochemistry.

In the study of the solid state, while we draw continually on knowledge of properties of isolated constituents such as those discussed above, we have also to recognise the great importance of interactions between the now closely-neighbouring molecules and ions. These interactions are reflected in the optical, electrical, thermal, and mechanical properties of the solids. The distinction between intermolecular and intramolecular influences is often hard to draw and there arise ambiguities which blur the distinction between ionic and covalent lattices. Modern solid-state theory, with its emphasis on the crystal as a whole, offers unifying principles by which to interpret the crystalline state. Chief among them is the universal relevance of the electron-energy diagram. In its terms, thermal decompositions, photoconductivity, photolysis, and absorption spectra find a consistent, unifying interpretation. The ideal crystalline lattice forms the basis for this theory in its simplest form.

Real crystals, however, are not perfect infinite lattices. Crystal surfaces, inhomogeneities, point defects, and dislocations sharply influence both the energy levels available for electrons and the probabilities for growth of new phases, so that the interpretative problems posed by the defect ionic azide lattice are subtle and difficult. The present state of the study of azide

¹ Audrieth, *Chem. Rev.*, 1934, **15**, 169.

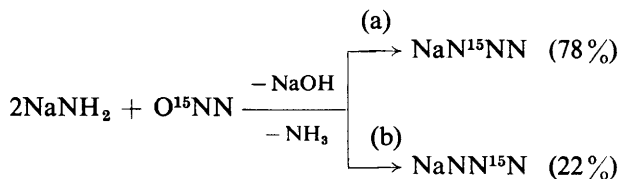
² Evans, Yoffe, and Gray, *Chem. Rev.*, 1959, **59**, 515.

crystal decompositions is confused but encouraging. The role of point defects at least is becoming clearer, and, when their influence has been assessed precisely, that of dislocations will be less formidable to unravel.

Azides explode. Such transformations are far from isothermal, and are correspondingly more complex than the slow thermal decompositions and photolyses. Self-supporting ignition, often having the attributes of a reproducible steady burning, may also accelerate so that burning is superseded by a violent detonation, traversing the crystal at enormous speed, and associated with an intensely ionised plasma that is far from thermal equilibrium. These phenomena are the pinnacles of difficulty in the azide domain. When they cannot be ascended from a base of first principles, they may be surveyed from the vantage points of isothermal kinetics and the theory of thermal explosions. Their brief description and discussion forms the end of this Review.

2. Preparation*

The common laboratory source of azides is technical sodium azide, which is manufactured from sodamide and nitrous oxide. The course of this reaction has been investigated by Clusius *et al.*,³ using [¹⁵N] nitrous oxide. The results for sodamide did not indicate a single reaction pathway; although 78% of the middle azide nitrogen comes from the middle atom of nitrous oxide, 22% comes from the terminal nitrogen. For the corresponding reaction with calcium amide, however, the former path (a) was followed almost exclusively (99%).



In further preparations, hydrogen azide (which, unfortunately, is both explosive and poisonous) is the common intermediate.^{1,2} Some of the dangers of distillation can be avoided by ion-exchange techniques. Some azides may be prepared from aqueous solutions; for others, dry reactants are necessary and ethereal solutions useful. Recently, the metal hydrides and alkyls have been treated with hydrogen azide⁴ and the range of known azides extended by the synthesis of anhydrous BeN₆, BN₉, MgN₆, AlN₉, SiN₁₂, GaN₉, and SnN₁₂, and other (complex) azides.

* This section is intended only to touch on recent aspects; for details of standard preparations see refs. 1 and 2 and standard works.

³ Clusius *et al.*, *Helv. Chim. Acta*, 1955, **38**, 1834, 1843; 1956, **39**, 681; 1958, **41**, 972, 2265.

⁴ Wiberg and Michaud, *Z. Naturforsch.*, 1954, **9**, 495.

3. Structure

In this section, only the internal (intramolecular) structures (of covalent azides, of the azide ion, and of the azide radical) are considered. Inter-molecular (and interionic) interactions are considered along with other properties in Section 5.

(a) **Covalent Azides.**—The only complete structural determinations on gaseous azide molecules are those of HN_3 (and DN_3) and methyl azide. Historically, solid cyanuric triazide was the first to be studied. The bond lengths and interbond angles⁵ are shown in Fig. 1; beside them are included values for some related nitrogen derivatives.

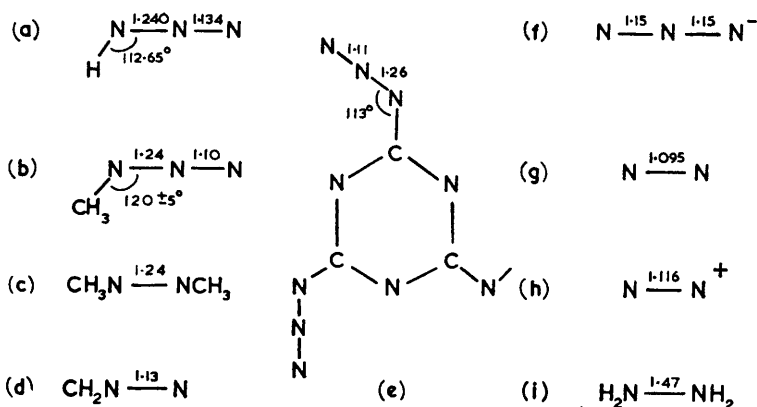


FIG. 1. Bond-lengths and interbond angles in some azides and related compounds. (a) Hydrogen azide, (b) methyl azide, (c) azomethane, (d) diazomethane, (e) cyanuric triazide, (f) azide anion, (g) nitrogen, (h) nitrogen molecular ion, (i) hydrazine.

The covalent azides share with the azide ion a collinear (N–N–N) arrangement of nitrogen atoms [see under (b) below], but possess a non-collinear terminal X–N bond. (This also appears to be the case for silyl azide, not yet completely investigated.) The N–N distances are unmistakably differentiated: the HN–N_2 bond is 1.24 Å, like the N–N bond of azomethane; the $\text{N–N}_2\text{H}$ bond is much contracted (1.134 Å), lying close to that (1.13 Å) in diazomethane and that (1.116 Å) in the “ $2\frac{1}{2}$ -bonded” ion N_2^+ , though it is appreciably longer than the triple bond in the N_2 molecule.²

The vibrational spectrum and force constants⁶ reflect the same pattern. When valence-bond force constants are evaluated from the six normal vibrations of NH_3 (and DN_3) the two stretching force constants (in 10^5 dyne cm.^{-1} units) are: k_1 (HN–N_2) = 10.1; k_2 ($\text{HN}_2\text{–N}$) = 17.3.

⁵ “Tables of Interatomic Distances and Configurations of Molecules and Ions,” ed. Sutton, Chem. Soc. Special Publ. No. 11, 1958.

⁶ Gray and Waddington, *Trans. Faraday Soc.*, 1957, 53, 901.

(b) **The Azide Ion, N_3^- .**—Knowledge of the size and shape of the azide ion comes from *X*-ray crystallographic studies, which are discussed in Section 5(b). In the inorganic salts the ion is linear and symmetrical, approximating in shape to an ellipsoid of revolution with axes *ca.* 5.1, 3.5, and 3.5 Å. The nuclei embedded in this electron-cloud are *ca.* 1.15 Å apart, a distance intermediate between a double and a triple bond but close to those in N_2^+ and diazomethane. The non-spherical distribution of charge has been represented by the superposition of a central point charge ($-e$) and a linear quadrupole (having $-0.83e$ at each terminal N and $+1.66e$ at the centre). The anisotropy of the electron-distribution shows up in optical properties [section 5 (c)].

Intra-ionic vibration frequencies [see 3(c)] lead to values (10^5 dyne cm^{-1}) for the force-constants of the general quadratic force field: for stretching, $k_1 = 13.36$; for bending, $k_\delta l_1^{-2} = 0.58$; for the stretching-stretching interaction, $k_{11} = 1.74$.

The isolated gaseous ion, which has been detected in mass-spectrometric studies, is likely to have the same structure. It has 16 electrons, like the cyanamide ion, NCN^{2-} , and carbon dioxide, and thus a $^1\Sigma_g^+$ ground state and a pattern of molecular orbitals resembling those of CO_2 (with, *e.g.*, the uppermost electron pair in a non-bonding orbital) is to be expected for N_3^- . Knowledge of excited states is potentially very important in interpretation of optical absorption spectra [section 6(b)] and in identifying energy levels in crystalline azides.

(c) **The Azide Radical, $\cdot N_3$.**—The azide radical, $\cdot N_3$, is isoelectronic with the cyanate radical, $\cdot NCO$, and with the positive molecular ions CO_2^+ and N_2O^+ ; all four species have been detected^{7,8} spectroscopically. Like CO_2^+ , it is expected to be linear and to have an “inverted” $^2\Pi_g$ ground state. Just as removal of an electron from the non-bonding orbital causes only slight alterations in the bond lengths, vibration frequencies, and force constants of carbon dioxide, so the azide radical may also be expected in these respects to resemble the azide ion fairly closely. Estimated values for ν_1 , ν_2 , and ν_3 are 1250, 600, and 2000 cm^{-1} ; values of 2150—2140 and of 1700 cm^{-1} have been reported^{9,7} for ν_3 .

A species $N \dots N_2$, distinct from N_3 as concerned above, has been invoked¹⁰ in studies of nitrogen atoms formed in a nitrogen discharge and trapped in a solid nitrogen matrix at 4°K. The relation of these species to the free nitrogen atom on the one hand and the azide radical on the other is under discussion.

⁷ Thrush, *Proc. Roy. Soc.*, 1956, *A*, **235**, 143.

⁸ Dixon, *Phil. Trans.*, 1960, *A*, **252**, 165; *J. Chem. Phys.*, 1959, **31**, 258; Holland, Dixon and Style, *Nature*, 1958, **182**, 336; Mrozowski, *Phys. Rev.*, 1947, **72**, 682, 691; Callomon, *Proc. Chem. Soc.*, 1959, 313.

⁹ Pimentel, *et al.*, *J. Chem. Phys.*, 1956, **25**, 1080; 1957, **26**, 145.

¹⁰ Peyron, Hörl, Brown, and Broida, *J. Chem. Phys.*, 1959, **30**, 1304; Vanderslice, Mason, and Lippincott, *J. Chem. Phys.*, 1959, **30**, 129.

(d) **Covalent and Ionic Character in the Azides.**—From the foregoing, the structural distinctions between hydrogen azide and the alkali-metal azides appear to offer a simple and clear distinction between covalent and ionic azides: the ionic azide has a symmetrical N–N–N group with identical terminal atoms, while the terminal atoms of covalently bound azides are differently placed and the group is not symmetrical.

It is to be expected that, when the solid-state and interionic interactions are examined, the distinction drawn here will require modification in order to deal with subtler differences.

4. Thermochemistry

The strengths of different chemical bonds greatly influence the course of chemical reactions. To interpret the chemistry of the azides, it is necessary to have values for the dissociation energies of the bonds they contain. In this section we first deal with the heats of formation of the covalent azides, including hydrogen azide, and then with the heats of formation of the azide radical and the azide ions. Finally, reaction thermochemistry is discussed, and the participation of excited species considered with it. As before, we are concerned with isolated species, *i.e.*, with reactions in the gaseous state; the thermodynamics and thermochemistry of crystals, since they involve intermolecular forces, are dealt with subsequently. Lattice energies are considered with other properties of the ideal crystal [see 5(b)], and decomposition heats with thermal decomposition (section 7).

(a) **Heats of Formation of Covalent Azides.**—A good value for the heat of formation of hydrogen azide has been potentially available since 1892, when Berthelot and Matignon¹¹ measured the heat of combustion of ammonium azide. However, from 1893 until recently it has been obscured by an arithmetical error introduced by Berthelot in the course of "corrections" applied to the original data. Today, the most reliable values come from the titration heats of Gray and Waddington,¹² and the explosion heats of Gunther, Mayer, and Müller-Skjöld.¹³ Hydrogen azide is a very endothermic gas ($\Delta H_f^\circ = 71.66$ kcal. mole⁻¹) and a weak acid^{1,2} in aqueous solution, with $10^5 K_a$ (mole l.⁻¹ at 20°) equal to 2.1 for HN₃ in H₂O and 0.98 for DN₃ in D₂O.¹⁴ The other thermodynamic properties of gaseous HN₃ as an ideal gas have been calculated from spectroscopic data by Dows and Pimentel.¹⁵ At 25° they calculate that (in cal. deg.⁻¹ mole⁻¹) $S^\circ = 57.083$ and $C_p = 10.443$.

For phenyl azide (1929), ethyl azidoacetate (1929), cyanuric triazide (1952), 2-triazoethanol (1953), cyclopentyl azide (1954), and cyclohexyl

¹¹ Berthelot and Matignon, *Ann. chimie et physique*, 1892, **27**, 289; 1893, **28**, 126.

¹² Gray and Waddington, *Proc. Royal Soc.*, 1956, *A*, **235**, 106.

¹³ Gunther, Mayer, and Müller-Skjöld, *Z. phys. Chem.*, 1935, **175**, 154.

¹⁴ Bunn, Dainton, and Duckworth, *Trans. Faraday Soc.*, 1961, **57**, 1131.

¹⁵ Dows and Pimentel, *J. Chem. Phys.*, 1955, **23**, 1258; see also Eyster and Gillette, *ibid.*, 1940, **8**, 369.

azide (1954) there are experimental values² of standard heats of formation (dating from the years indicated). A convenient means of testing the consistency of these and of applying the information they contain to the evaluation of enthalpies of formation of other azides proceeds through the evaluation of group energy terms. This treatment* (using Franklin's values¹⁶ for energy terms of common groups) leads to $H(-N_3) = ca. 71$ kcal. mole⁻¹ as the contribution of an azide group to the standard heat of formation at 25° of a gaseous azide from its elements in their standard states. However, the data are far from consistent and such an estimate is useful only as a rough guide.

(b) **Heats of Formation of N_3^- , $\cdot N_3$, and N_3^+ .**—The thermochemistry of the members of this group is linked "internally" by the electron affinity¹⁷ and ionisation potential of the azide radical and "externally" by the dissociation energies of azide bonds ($X-N_3$).

(i) *Enthalpy of formation, Q_- , of the gaseous azide anion N_3^- .* The most direct (but not the most accurate) value for $Q_- = \Delta H_f(N_3^-, g)$ comes from electron-impact measurements¹⁸ on hydrogen azide, which lead to a (crude) upper limit, $Q_- \leq 45 \pm 5$. If the heat of formation of methyl azide were known, another estimate of Q_- would be possible from similar experimental results.

The most reliable value for Q_- comes from the application of the Born cycle to the ionic azides, and depends on knowledge¹⁹ of their lattice energies, W_L :

$$Q_- = W_L(MN_3) + 2RT - (I + L)_M + \Delta H_f^\circ(MN_3)$$

The mean value (determined¹⁹ from five azides) is $Q_- = 34.8 \pm 0.1$ kcal. mole⁻¹.

(ii) *The electron affinity, E , of the gaseous azide radical.* There are three independent sources for E and they lead to a "best" average value of $ca. 70 \pm 5$ kcal. mole⁻¹.

Appearance-potential measurements for ionisation and electron-capture reported¹⁸ for methyl azide lead to values for $A(Me^+)$ and $A(N_3^-)$ so that if no kinetic energy is involved we have

$$E(N_3) = A(Me^+) - A(N_3^-) - I(Me) = 69 \pm 7 \text{ kcal. mole}^{-1}.$$

Charge-transfer spectra yield¹⁹ two further values. The (ultraviolet)

* I am indebted to Dr. M. J. Pearson of Seattle for carrying out these calculations.

¹⁶ Pearson and Gray, 1960, to be published; Pearson, Ph.D. Dissertation, Leeds, 1962.

¹⁷ Mulliken (quoted in ref. 38).

¹⁸ Franklin, Dibeler and Morris, *J. Res. Nat. Bur. Stand.*, 1958, **61**, 41; Franklin, Dibeler, Reese, and Krauss, *J. Amer. Chem. Soc.*, 1958, **80**, 298.

¹⁹ Gray and Waddington, *Proc. Royal Soc.*, 1956, *A*, 235, 481.

absorption spectrum of aqueous sodium azide²⁰ has an inflexion at 2240 Å identifiable with absorption arising from transfer of an electron from the ion to the water. The (visible) absorption spectrum^{14,19,21} of the ion-pair (azide + ferric) has a maximum at 4600 Å, identifiable with absorption arising from transfer of an electron from the azide to the ferric ion. These two observations lead, respectively, to $E = 67 \pm 5$ and $E = 73 \pm 5$ kcal. mole⁻¹.

(iii) *Enthalpy of formation, Q , of the gaseous azide radical.* The value of $Q = \Delta H_f^\circ (\cdot N_3, g)$ comes from the combination $Q = E + Q_-$. These constituents have been discussed above; they lead to $Q = ca. 105 \pm 3$ kcal. mole⁻¹. A semi-empirical quantum-mechanical study²² by Singh leads to $Q = 113$ kcal. mole⁻¹.

(iv) *Ionisation potential, I , of the azide radical, and the enthalpy of formation, Q_+ , of the positive azide ion N_3^+ .* An upper limit for the enthalpy of formation of the ion N_3^+ is set by the value¹⁸ of its appearance potential (16.0 ± 0.2 v) from HN_3 as $Q_+ \leq 388 \pm 5$ kcal. mole⁻¹.

The ionisation potential $I(N_3)$, derived by combining the enthalpies of formation Q_+ and Q of ion and radical, is $I = (Q_+ - Q) \leq 283 \pm 6$ kcal. mole⁻¹.

(v) *Electronegativity of the azide radical.* The values found for I and E place the azide ion, with $(I + E)/(130 \text{ kcal.}) = 2.71$, between the bromide ion (with $x = 2.8$) and the iodide ion (with $x = 2.5$) on Mulliken's electronegativity scale.¹⁷

(c) Reaction Thermochemistry and Bond-dissociation Energies.—These thermochemical magnitudes form the basis for the reaction thermochemistry of the azides and for the evaluation of the dissociation energies of the bonds they contain. This section is thus both the completion of the development for the covalent azides and the starting point for the study of energetics of the solids.

Fig. 2 summarises some of the energy relationships^{2,19} between species in their ground states. The numerical values are those appropriate to HN_3 , but similar relative relations are to be expected for covalent azides, XN_3 , in general.

(i) *Hydrogen azide.* Dissociation of the H-N bond² requires 85 kcal. mole⁻¹. This value lies in the region of other H-N bonds; in ammonia, $D(H-NH_2) = 104 \pm 2$, and in imino, $D(H-N) = 82 \pm 3$ (whence, in amino, $D(H-NH) = 94 \pm 5$).

Except insofar as a chain reaction could ensue, thermal decomposition is unlikely to involve unimolecular fission of the H-N₃ bond. The expected

²⁰ Bonnemay and Verdier, *Compt. rend.*, 1950, **230**, 2300; Duckworth, 1957, personal communication.

²¹ Badoz-Lambling, *Bull. Soc. chim. France*, 1950, 1195; Santhappa, *J. Madras Univ.*, 1954, **24b**, 91; El Shami and Sherif, *Egypt. J. Chem.*, 1958, **1**, 35.

²² Singh, *Proc. Roy. Soc.*, 1954, *A*, **225**, 519.

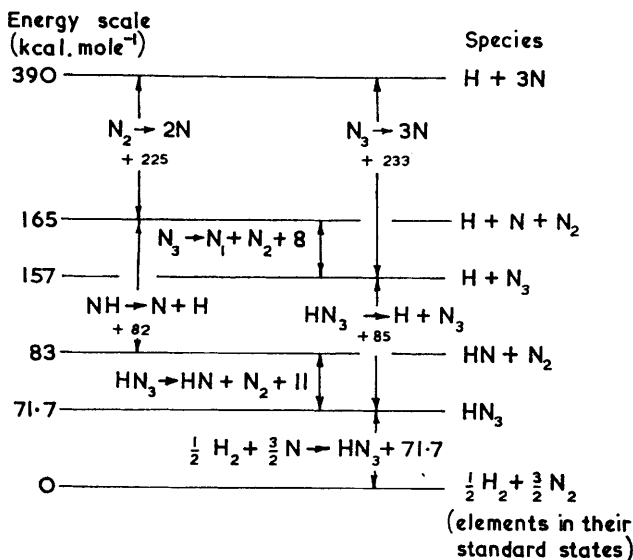
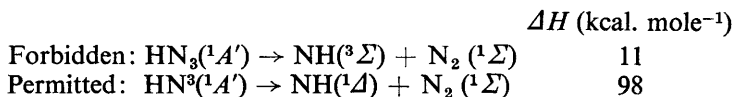
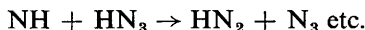


FIG. 2. Energy relationships (ΔH) in hydrogen azide and the azide radical; all entries refer to gaseous species at 25° in their ground states.

path of thermal decomposition is through the imino-radical.²³⁻²⁶ Unimolecular decomposition by this pathway would need only 11 kcal. mole⁻¹ if all the species were in their ground states; but that, however, is a forbidden combination. If excited states of NH are invoked, then, for the easiest permitted reaction, about 98 kcal. mole⁻¹ are required



This figure is a minimum for the activation energy of unimolecular HN-N₂ bond fission, and hence, if that step is rate-controlling, for the decomposition of HN₃. If, however, hydrogen abstraction reactions follow, the mechanism will be complex:



Such steps are suggested by the formation of ammonia from the (heterogeneous) thermal decomposition²⁶ and from the photolysis^{7,25} of hydrogen azide. The explosion^{13,27} yields only hydrogen and nitrogen.

²³ Pannetier and Gaydon, *J. Chim. phys.*, 1951, **48**, 221; *Bull. Soc. chim. France*, 1954, 1068; *Compt. rend.*, 1955, **240**, 958.

²⁴ Rice and Frearno, *J. Amer. Chem. Soc.*, 1951, **73**, 5529; 1953, **75**, 548; Mador and Williams, *J. Chem. Phys.*, 1954, **21**, 1627; Whittle, Dows, and Pimentel, *ibid.*, 1954, **21**, 1943; 1955, **22**, 1606.

²⁵ Meyer and Schumacher, *Z. phys. Chem.*, 1934, **170a**, 33.

²⁶ Leermakers, *J. Amer. Chem. Soc.*, 1933, **55**, 2719.

²⁷ Gray and Waddington, *Nature*, 1957, **179**, 570.

(ii) *Organic azides.* Only a rough average, $D(\text{R-N}_3) = 72 \pm 8$ kcal. mole⁻¹, can be deduced from the thermochemical data available² for the carbon-nitrogen bond-dissociation energy. This is large enough to rule it out as a likely step in normal low-temperature pyrolysis. As is to be expected, organic azides decompose preferentially by RN-N_2 bond-fission: this is further discussed in Section 7(a). In phenyl azide²⁸ and fluorine azide pyrolysis, the formation of azobenzene and difluorodiazene, respectively, offers striking chemical evidence for this path.



In the gas phase, the formation of ethylenimine from ethyl azide suggests the occurrence of disproportionation and similar reactions.

(iii) *The azide radical.* Although extensive participation of the azide radical in the gas-phase during isothermal decomposition of covalent azides is unlikely, its presence has been detected⁷ in (non-isothermal) flash photolysis in the gaseous phase. Its prime importance as a chemical intermediate lies however in its role in the decomposition of solids [section 7(b)].

Unimolecular decomposition of the azide radical (from its ${}^2\Pi_g$, ground state) to form a molecule and an atom of nitrogen also in their ground states requires only *ca.* 7.5 kcal. mole⁻¹. This, however, is another "forbidden" reaction and the energy needs of the first "permitted" reaction are at least 62 kcal. mole⁻¹.

| | ΔH (kcal. mole ⁻¹) |
|---|--|
| Forbidden: $\text{N}_3({}^2\Pi_g) \rightarrow \text{N}({}^4S) + \text{N}_2({}^1\Sigma)$ | 7.5 \pm 3 |
| Permitted: $\text{N}_3({}^2\Pi_g) \rightarrow \text{N}({}^2D) + \text{N}_2({}^1\Sigma)$ | 62.3 \pm 3 |
| Permitted: $2\text{N}_3({}^2\Pi_g) \rightarrow 3\text{N}_2({}^1\Sigma)$ | -210 \pm 6 |

Reaction in pairs, however, is not forbidden by spin conservation rules and, thermochemically, is highly favourable; it is probably the main route by which molecular nitrogen is formed from azide radicals. An instance occurs in the electrolysis of aqueous azides. Clusius and Schumacher²⁹ electrolysed aqueous potassium azide having the isotopic composition ${}^{14}\text{N}{}^{15}\text{N}{}^{14}\text{N}$. They found at the anode no ${}^{15}\text{N}_2$ but ${}^{14}\text{N}_2 + 2 {}^{14}\text{N}{}^{15}\text{N}$, a result consistent with an N_6 intermediate having either an extended (pseudo-halogen) or an annular structure.

5. Azides in the Solid State

The discussion up to now has emphasised the atomic or molecular aspect. From this viewpoint, azide crystals are divisible into molecular lattices and ionic lattices according to the units of which they are constructed. In the molecular lattice, only relatively weak, short-range forces exist between the molecules, which are accordingly expected to possess

²⁸ Russell, *J. Amer. Chem. Soc.*, 1955, **77**, 3487.

²⁹ Clusius and Schumacher, *Helv. Chim. Acta*, 1958, **41**, 972.

the same asymmetric $X-N-N'-N''$ structure as does the isolated molecule in the gas. In the ionic lattice, on the other hand, where the charged constituents are expected to arrange themselves to satisfy the requirements of stoichiometry and electrostatic energy, the symmetry of the electrostatic field is tacitly assumed not to affect perceptibly the symmetry of the azide ions. Thus, from the "atomic" viewpoint, intramolecular bond-lengths offer themselves as obvious criteria of valency type. Although it must be noted that many potentially "borderline" structures (among them lithium and beryllium azides, aurous azide, mercurous and mercuric azides) have not been determined and that no azide structure has as yet been determined to the limits of present-day precision, there is no difficulty on this basis in dividing all those azides for which complete structures are at present known into two classes: all the metal azides (including ammonium azide) are ionic; hydrogen azide and all other azides are covalent.

The disadvantage of the atomic viewpoint is that it is too simple. The difficulties are most troublesome when deviations from basically ionic structures are involved. Thus, chain- and layer-structures are known to exist, but the directional forces needed to produce them cannot have their origin in simple electrostatic valency. Another indication of departures from a localised ionic structure is the occurrence of abnormally high refractive indices. Fundamentally, it is the idea of the ionic unit as a self-contained, 16-electron entity which is at fault, although it is an invaluable approximation. The quantum theory of solids, from which have come the most fruitful advances in interpreting their physics and chemistry, emphasises the energy levels of the crystal as a whole and this is the viewpoint which must be adopted to perceive the pattern of azide reactivity more clearly.

Quantitatively, the quantum theory of ionic solids rests on knowledge of their structure and their thermochemistry and these are the aspects which must next receive attention. When they have been surveyed, the pattern of electron energy levels in the ideal crystalline azides may be presented.

(a) Crystal Structures of Ionic Azides.—The dominant factors determining the lattice geometry (and the electron density) of the various ionic azides are the shape of the azide anion, and the charge, size, and ionisation potential of the cation. These factors are reflected in the morphology and optics of the crystals, and above all by their X -ray-, electron-, and neutron-diffraction patterns. It is convenient to consider separately the azides of univalent and bivalent cations and, since it is common to all families, to discuss the shape and size of the azide anion first.

(i) *Size and shape of the azide anion in ionic crystals.* Gray and Waddington¹⁹ showed that the azide ion could be adequately represented as an ellipsoid of revolution with major and minor semi-axes 2.54_5 and 1.76_5 Å, respectively. (These dimensions, chosen to fit the observed dimensions of KN_3 are also consistent with the isomorphous structure of rubidium

and caesium azides and with the appearance of a different structure for sodium azide.) Reported values for the N-N distances vary from 1.12 to 1.17 Å but the errors of measurement are such that differences from one azide to another are not significant. There is no firm evidence for non-linearity or departure from equality of N-N distances, though the older literature contains some discordant reports. The azides are isomorphous with the difluorides and, less consistently, with the (isoelectronic) fulminates, cyanates, and thiocyanates.

TABLE 1. *Crystal structures of univalent ionic azides, MN₃.*

| Salt | Crystal class | Cell constants (Å) |
|--------------------------------|---------------------------|------------------------------------|
| NaN ₃ | Body-centred rhombohedral | a_0 5.488, α 38° 43' |
| KN ₃ | Body-centred tetragonal | a_0 6.094, c_0 7.056 |
| RbN ₃ | Body-centred tetragonal | a_0 6.36, c_0 7.41 |
| CsN ₃ | Body-centred tetragonal | a_0 6.72, c_0 8.04 |
| NH ₄ N ₃ | Orthorhombic | a_0 8.93, b_0 8.64, c_0 3.60 |
| TlN ₃ | Body-centred tetragonal | a_0 6.23, c_0 7.37 |
| AgN ₃ | Orthorhombic | a_0 5.59, b_0 5.91, c_0 6.01 |
| CuN ₃ | Tetragonal | a_0 8.65, c_0 5.59 |

| Salt | Mols. per unit cell | Co-ordination | N _I -N _{II} | X-N _{II} | Ref. |
|--------------------------------|---------------------|---------------|---------------------------------|-------------------|------|
| NaN ₃ | 1 | 6:6 | 1.17 | 2.48 | 30 |
| | | | 1.15 ± 0.016 | | 31 |
| KN ₃ | 4 | 8:8 | 1.16 | 2.96 | 30 |
| | | | 1.145 ± 0.017 | | 31 |
| RbN ₃ | 4 | 8:8 | 1.13 | 3.11 | 32 |
| CsN ₃ | 4 | 8:8 | — | 3.34 | 33 |
| NH ₄ N ₃ | 4 | 8:8 | 1.166 | 3.2 | 31 |
| | | (4 closer in) | | 2.98 | |
| TlN ₃ | 4 | 8:8 | — | 2.98 | 34 |
| AgN ₃ | 4 | 8:8 | 1.16 | 2.79 | 35 |
| | | (4 closer in) | | 2.56 | |
| CuN ₃ | 8 | 4:4 | 1.17 | 2.23 | 36 |

(ii) *The univalent azides MN₃.* The common univalent azides are: NaN₃, KN₃, RbN₃, and CsN₃ from group IA; CuN₃ and AgN₃ from group IB; TlN₃ from group IIIB; and NH₄N₃. Crystal structures of all these have been determined.³⁰⁻³⁶ Their interpretation in terms of ionic size and shape

³⁰ Hendricks and Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904.

³¹ Frevel, *Z. Krist.*, 1936, **94**, 197; *J. Amer. Chem. Soc.*, 1936, **58**, 779.

³² Gunther, Porger, and Rosbaud, *Z. phys. Chem.*, 1930, **6b**, 459.

³³ Waddington, Ph.D. Dissertation, Cambridge, 1955.

³⁴ Handbook of Chemistry and Physics, 40th edn., Chemical Rubber Publishing Co., Cleveland, Ohio; Yoffe, unpublished work; Krause, personal communication.

³⁵ Pfeiffer, Ph.D. Thesis, California Inst. of Technology, 1948; Hughes and Pfeiffer, ASXRED meeting, Cornell, 1949; West, *Z. Krist.*, 1936, **95**, 421.

³⁶ Wilsdorf, *Acta Cryst.*, 1948, **1**, 115.

and the influence of ionisation potential has been considered by Evans and Yoffe.³⁷

Size. The influence of the size of the cation (relative to that of N_3^-) is apparent in the alkali-metal azide series. The azides of the larger cations (K, Rb, Cs) all show eight-fold co-ordination (body-centred tetragonal arrangements) and in them, increase in the lattice dimensions a_0 and c_0 follows the increase in cationic radius. In sodium azide, with its smaller cation, the co-ordination changes to 6:6 in a body-centred rhombohedral structure, in which the azide ions are aligned with their long axes parallel.

Shape. The influence of the shape of the cation is apparent in NH_4N_3 . Its crystals are orthorhombic³¹ (it is isomorphous with NH_4HF_2) and it has four azide groups drawn in more closely to each ammonium ion. Four others are slightly further away. A ready interpretation⁶ is here available in terms of hydrogen-bonding; when we encounter the similar features in AgN_3 we have to consider a different origin for the appearance of cationic "shape", *i.e.*, for the departure from spherical symmetry of purely ionic bonding.

Ionisation potential. Ionisation potential is not unrelated to ionic radius but a strong separate influence can often be discerned. Ionic radii (see annexed Table) are very similar for Na^+ and Cu^+ , for K^+ , Ag^+ , and NH_4^+ , and for Rb^+ and Tl^+ , but ionisation potentials³⁸ divide the atoms differently; the alkali metals have "low" values, thallium an "intermediate" value, and copper, silver, and gold "high" values.

| | Li | Na | K | Rb | Cs | Cu^+ | Ag | Au^+ | Tl^+ |
|---------------------------|------|------|------|------|------|--------|------|--------|--------|
| Ionic radius (a.u.) | | 0.95 | 1.33 | 1.48 | 1.69 | 0.96 | 1.26 | | 1.51 |
| Ionisation potential (v)* | 5.39 | 5.12 | 4.32 | 4.16 | 3.87 | 7.68 | 7.54 | 9.233 | 6.07 |

* 1 electron-volt = 23.06 kcal. mole⁻¹.

In crystal structure, sharp differences are found between orthorhombic (6:6 co-ordinated) NaN_3 and tetragonal (4:4 co-ordinated) CuN_3 with chains of cuprous and azide ions and a reduced M-N distance. Silver azide is distorted from the potassium azide lattice in the same way as ammonium azide; the M-N distance has its normal "ionic" value for the outer group of four azides but is abnormally short for the inner group. Thallous azide, though isomorphous with RbN_3 , has M-N distances which are abnormally short.

These discrepancies are the structural symptoms of deviations from purely ionic bonding. Refractive index and optical absorption measurements [see section 5(c)] augment this evidence. Thus, the alkali-metal azides are colourless and have low refractive indices typical of discrete ions, while thallous, silver, and cuprous azide are either coloured or

³⁷ Evans and Yoffe, *Proc. Royal Soc.*, 1957, A, 238, 568.

³⁸ Pauling, "The Nature of the Chemical Bond," 2nd edn., Oxford Univ. Press, London, 1960; Wells, "Structural Inorganic Chemistry," 3rd edn., Oxford Univ. Press, London, 1960.

absorb in the near-ultraviolet region, and their refractive indices vary greatly in different directions with maximum values greater than 2 (*ca.* 4 for AgN_3). The signs are those of a delocalisation of the electrons in preferred directions. In atomic terms, one might describe the process as a partial return of an electron from the azide anion to its parent metal atom and, insofar as the electron may enter a non-spherically symmetric orbit (*e.g.*, in Tl), one may regard the imperfectly ionised metal as possessing shape. This is the origin of the somewhat extravagant statements³⁸ of Pauling and of Wells that "the heavy metal azides are essentially covalent compounds" and of Pfeiffer³⁵ that "the bonding in silver azide is covalent within sheets of molecules and van der Waals between sheets." Since the term "covalent azide" has already a useful but different significance, it is perhaps preferable here to keep to non-committal phrases such as "delocalised" when discussing solid inorganic azides. The semantic difficulties arise from the atomic viewpoint.

(iii) *Bivalent azides*, MN_6 . No less interesting and important, but both more complex and less thoroughly investigated, are the bivalent azides (Table 2). Only SrN_6 has been examined fully, though crystal classes and cell constants have been determined for CuN_6 , CaN_6 (isomorphous with SrN_6), BaN_6 , CdN_6 , and PbN_6 (two forms). In strontium azide³⁹ the azide

TABLE 2. *Crystal structures of bivalent ionic azides, MN_6 .*

| Salt | Crystal class | Cell constants (Å) | | | Mols. per unit cell | Ref. |
|---------------------------|---------------|--------------------|----------|------------------------|---------------------|---------|
| | | <i>a</i> | <i>b</i> | <i>c</i> | | |
| CaN_6 | Orthorhombic | 11.62 | 10.92 | 5.66 | 8 | 33 |
| SrN_6 | Orthorhombic | 11.82 | 11.47 | 6.08 | 8 | 39 |
| BaN_6 | Monoclinic | 9.63 | 4.36 | 5.54, α 97°52' | 2 | 40 (32) |
| CdN_6 | Orthorhombic | 7.82 | 5.46 | 7.02 | 8 | 41 |
| α - PbN_6 | Orthorhombic | 6.63 | 11.31 | 16.25 | 12 | 42, 43 |
| β - PbN_6 | Monoclinic | 18.49 | 8.84 | 5.12, α 107°35' | 8 | 44 (43) |
| CuN_6 | Orthorhombic | 9.23 | 13.23 | 3.07 | 8 | 45 |

ions are linear and symmetrical. Each strontium ion has eight neighbours which can be classified in two groups of four. In the first group, the Sr-N separation (Å) is 2.63, and in the second 2.77. Since the ionic radius of strontium is 1.13 a.u., only the outer group can be looked on as purely ionically bound (azide contact radius $1.63 = 2.77 - 1.13$ Å); the smaller

³⁹ Llewellyn and Whitmore, *J.*, 1947, 881.

⁴⁰ Whitmore, 1945 (personal communication from Dr. E. G. Cox, 1959).

⁴¹ Bassière, *Compt. rend.*, 1935, **201**, 735; 1937, **204**, 1573; *Mem. serv. chim. de l'Etat*, 1943, **30**, 33.

⁴² Azaroff, *Z. Krist.*, 1956, **107**, 362.

⁴³ Pfeifferkon, *Z. Naturforsch.*, 1948, **3a**, 364.

⁴⁴ Azaroff and Klems, American Crystallographic Association Meeting, Washington D.C., January 1960.

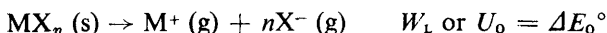
⁴⁵ Straumanis and Cirulis, *Z. anorg. Chem.*, 1943, **251**, 315; **252**, 9, 121.

Sr-N distance of 2.63 Å may, like that in AgN_3 , indicate the influence of directed bonding.

In the absence of complete structural data it is useful to consider what inferences may be made from knowledge³⁸ of ionisation potentials for metals forming bivalent ions. The annexed list shows some striking features, suggesting that the "heavy metal" azides should be rather strongly differentiated from the alkaline earth metal azides, and raising the expectation that, although LiN_3 is likely to be ionic, BeN_3 is not.

| | | | | | | | | |
|---------------------------------|--------|-------|-------|-------|-------|-------|-------|-------|
| | Be | Mg | Ca | Sr | Ba | Sn | Pb | Cr |
| First ionisation potential (v) | 9.320 | 7.644 | 6.111 | 5.692 | 5.21 | 7.332 | 7.415 | 6.76 |
| Second ionisation potential (v) | 18.206 | 15.03 | 11.87 | 9.95 | 9.95 | 14.5 | 14.96 | 16.6 |
| Radius of 2+ ion (Å) | 0.31 | 0.65 | 0.99 | 1.13 | 1.35 | — | 1.32 | — |
| | Mn | Fe | Co | Ni | Cu | Zn | Cd | Hg |
| First ionisation potential (v) | 7.43 | 7.896 | 7.86 | 7.633 | 7.72 | 9.39 | 8.99 | 10.43 |
| Second ionisation potential (v) | 15.7 | 16.16 | 17.3 | 18.2 | 20.34 | 17.89 | 16.84 | 18.65 |
| Radius of 2+ ion (Å) | 0.91 | 0.83 | 0.82 | 0.78 | — | 0.83 | 1.03 | 1.10 |

(b) **Lattice Energies.**—An important magnitude in the physics and chemistry of ionic solids is the lattice energy (U or W_L) defined as the increase in internal energy attending the separation of the oppositely charged constituents of the crystal.



Knowledge of W_L is needed in calculations of exciton levels, in the quantitative interpretation of absorption spectra and photo-conductivity, and in calculations of the energy required to form point defects.

Lattice energies are related to other thermochemical quantities by the extended Born-Haber cycle, given in Fig. 3 (for enthalpy changes at 25°) for MN_3 . Two independent relations may be read off the cycle:

(1) between lattice energy and ion-hydration heats

$$S - (H_+ + H_-) = W_L + 2RT \quad (1)$$

(2) between lattice energy and electron affinity, etc.

$$\Delta H_f^\circ + W_L + 2RT + E - I - L = Q - E \quad (2)$$

The importance of the Born-Haber cycle is that, once a reliable value for the lattice energy of one azide is established, it enables values for the

lattice energies of all azides to be obtained from their enthalpies of formation, etc.

Four routes to lattice energies are open (though not every one is applicable to every azide). First, there is the electrostatic, term-by-term calculation. This was used⁴⁶ by Jacobs for KN_3 , and refined by Gray and Waddington¹⁹ who took into account the appreciable contributions from the quadrupole moment [see section 3(b)] of the azide ion, and derived values for the lattice energies of KN_3 , RbN_3 , and CsN_3 . Secondly, there is

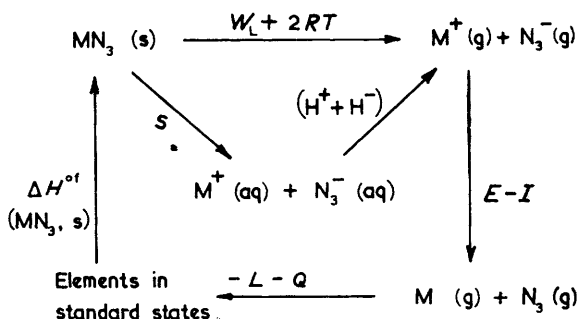


FIG. 3. Born cycle relating lattice energy to other thermochemical magnitudes; all entries refer to enthalpies at 25°.

the empirical relation of Kapustinsky¹⁹ (which, though valuable where complete calculations are impossible, gives values that are 2–3% too low for the azides). Thirdly, the relation (1) between hydration heats and lattice energy may be employed when combined ion-hydration heats are known; it yields good values for the azides of Li, Na, K, Rb, and Cs. Finally, there is the Born–Haber cycle [eqn. (2)] which employs known lattice energies in order to derive a “best” value for $(Q - E)$ or Q_- , the enthalpy of formation of the gaseous azide ion, and then uses this value of Q_- to derive unknown lattice energies. This is the origin¹⁹ of the entries in Table 3 for NH_4N_3 , CuN_3 , AgN_3 , TlN_3 , CaN_6 , SrN_6 , BaN_6 , and PbN_6 . As stressed elsewhere,² tabulation of a numerical value for a lattice energy neither requires nor implies the existence of ions in the lattices; much less does it signify wholly ionic bonding.

TABLE 3. Lattice energies of azides (kcal. mole⁻¹ at 25°); all values refer to internal energy.

| Azide | Lattice energy | Azide | Lattice energy | Azide | Lattice energy |
|----------------|----------------|-------------------------|----------------|----------------|----------------|
| LiN_3 | 194 | NH_4N_3 | 175 | CuN_3 | 227 |
| NaN_3 | 175 | CaN_6 | 517 | AgN_3 | 205 |
| KN_3 | 157 | SrN_6 | 494 | TlN_3 | 163.5 |
| RbN_3 | 152 | BaN_6 | 469 | PbN_6 | 434 |
| CsN_3 | 146 | | | | |

⁴⁶ Jacobs, Ph.D. Dissertation, London, 1954.

(c) **Other Properties of the Crystal Lattice.**—The optical, mechanical, thermal, and electrical properties of the crystal reflect with varying clarity the atomic structure and energetics of the lattice. A brief indication of characteristics must suffice here.

(i) *Optical properties.* Refractive index measurements^{2,30,47} have several applications. First, optical anisotropy indicates structural anisotropy, *i.e.*, in the disposition and orientation of the units of the lattice. When the equilibrium positions are known and the anisotropic contribution calculable, inferences about thermal motion may be made⁴⁸ from comparison with the measured birefringence. Secondly, unusually large refractive indices in certain directions indicate delocalisation of the electron; preferred directions of delocalisation may be revealed by measurements using polarised light. Thirdly, the magnitude of the refractive index is important in establishing⁴⁷ the separation of exciton levels [section 6(a)(ii)].

(ii) *Mechanical properties.* Work is sparse, but a good example of its relevance is the ready cleavage² of AgN_3 parallel to the 010 planes, supporting the idea of enhanced bonding within those planes.

(iii) *Thermal properties.* Measurements of most thermal properties (*e.g.*, heat capacities, thermal conductivities, and heats of fusion) are sparse and somewhat inaccurate. There are data^{1,2} for melting points, and interesting variations are shown by their values: KN_3 (*ca.* 350°); RbN_3 (*ca.* 320°); CsN_3 (*ca.* 325°); CuN_3 (205°); AgN_3 (250°); TiN_3 (335°). However, melting points are easier to measure than to interpret, since they relate to differences between solid and liquid phases, and little is known about the liquid phase:

$$T_f = (H_l - H_s)/(S_l - S_s)$$

All that can be definitely inferred from a low m.p. is a diminished stability of the crystal relative to the melt; m.p. and lattice energies do not vary in the same sense.

(iv) *Ionic conductance.* In a crystal, conductivity may arise from ionic or electronic conductance (or both). It is common for ionic conductance to involve the motion of only one ion; usually the cation is smaller and more mobile. Often, however, ionic mobility is confined to crystal surfaces. The bulk conductivity of potassium azide is probably⁴⁹ cationic; there is also a structure-sensitive surface contribution. Undecomposed silver azide is probably⁵⁰ a cationic conductor, silver ions moving by way of interstitial positions; conduction through partially decomposed silver azide is predominantly electronic.

⁴⁷ Bénard, in "Reactivity of Solids," ed. de Boer, Elsevier, Amsterdam, 1961, p. 362.

⁴⁸ G. E. Pringle, personal communication, 1962.

⁴⁹ Jacobs and Tompkins, *Proc. Royal Soc.*, 1952, *A*, **215**, 254.

⁵⁰ Tompkins *et al.*, *Discuss. Faraday Soc.*, 1957, No. 23, 202; *Proc. Roy. Soc.*, 1958, *A*, **246**, 197, 206.

(d) **Lattice Defects.**—It is convenient at this stage to list the ways in which real crystals deviate from ideal infinite lattices. Bénard⁴⁷ divides the imperfections into crystallographic and chemical, and the attached scheme indicates their inter-relation.

| <i>Crystallographic imperfections</i> | <i>Chemical imperfections</i> |
|---|--|
| External surface | Chemisorbed species |
| Internal surface | Foreign atoms at intercrystalline surfaces |
| { Stacking faults Dislocations (several kinds) Interstitial positions Vacant sites | } { Foreign atoms in interstices Foreign atoms on sites |

All these concepts [and others besides; see section 6(d)] have been invoked at various times in discussions of azide reactivity. Point defects and surfaces are the least mysterious; the roles of dislocations and stacking faults remain an enigma.

6. Electron Energy Levels in Crystalline Azides

Hitherto the discussion of structure has been concerned with the distribution of electrons through space. A distribution of a different kind—that of the electrons among the energy levels—has now to be considered.

(a) **Location of the Energy Levels.**—Various energy levels, or bands of levels, are available in the ideal azide lattice. The principal ones⁵¹ are the valence or full bands, the exciton levels, and the conduction bands. These are located at decreasing depths below the natural zero of energy (which is the energy of a free electron, at rest at infinity, outside the crystal). The description and location of these levels forms the subject of this section. Their importance resides in the unification of the physical properties (absorption spectra, photoconductivity, thermal and photoelectric emission) and in the basis they afford for the discussion [sections 7(a) and (b)] of photolysis and thermal decomposition.

(i) *Description and arrangement of energy levels.* In general, ionic azides are insulators. That is to say, even their most energetic electrons lie in a full band (the valence band) which is some considerable distance below the bottom of the conduction band. Between these two bands are the exciton levels. On the atomic picture, exciton formation corresponds to the excitation of an electron belonging to an azide anion to form a mobile entity, though, as an exciton has no net charge, its motion does not contribute to electrical conduction. An anion which has lost its electron completely (*e.g.*, to the conduction band) is said to form a positive hole in the

⁵¹ Mott and Gurney, "Electronic Processes in Ionic Crystals," Oxford University Press, London, 1948; Kittel, "Solid State Physics," Wiley, New York, 1956.

lattice because it is the site of a potential energy well; it also is mobile. An exciton is thus an electron bound by an approximately coulombic potential to a positive hole, and the different exciton levels correspond to the possible Bohr orbits, having their convergence limit at the level of the conduction band. There may also be lower-lying states of an excited anion [see section 6(b)] which do not possess mobility.

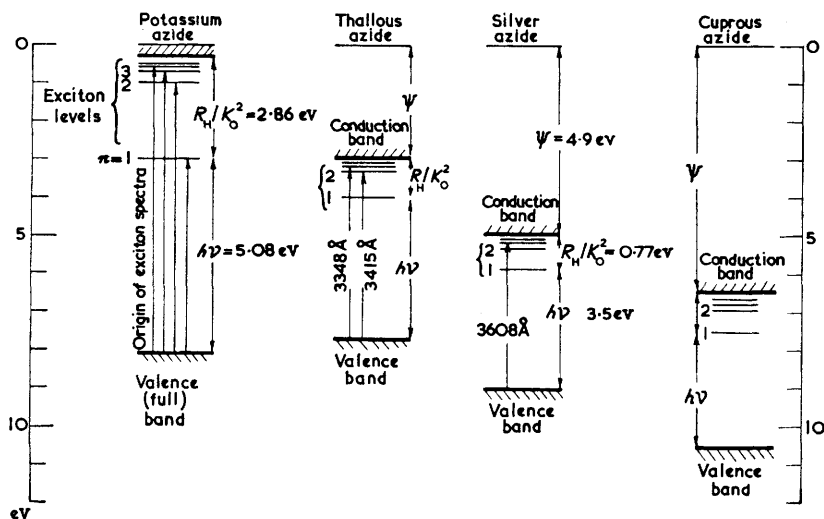


FIG. 4. Electronic energy levels (for optical transitions) for four crystalline ionic azides (energies in eV below the free state i.e., electron at rest at infinity); Ψ = work function; $h\nu$ = height of lowest exciton level above valence band; $R_H/K_0^2 \approx$ depth of lowest exciton level below conduction band ($F = 23.06$ kcal. per volt equiv.).

In Fig. 4 is presented a schematic energy-level diagram* for potassium, thallium(I), silver, and copper(I) azides. The magnitudes it displays are: (1) the height, $h\nu$, of the lowest exciton levels above the full (valence) bands; (2) the depth (ca. R_H/K_0^2) of the lowest exciton levels below the conduction band and the spacing of the exciton levels; (3) the distance from the bottom of the conduction bands to a level just below the top of the valence bands; (4) the depth Ψ of the bottom of the conduction bands below the common zero (energy of a liberated electron at rest at infinity). Their determination is briefly outlined.

(ii) *The spacing of the exciton levels.* It is possible to estimate the

* All the magnitudes correspond to "optical" excitations, i.e., to instantaneous processes in which the lattice does not have time to relax to a new equilibrium configuration. The relation of these to "thermal" magnitudes is discussed below. Numerical values are recorded to give a better indication of relative magnitudes; they are by no means the last word in accuracy, though not likely to be seriously misleading.

spacing of the exciton levels since, relative to the lower edge of the conduction band, they obey the quantisation:

$$\epsilon_n^{\text{opt.}} = -(m^*/m)(R_H/K_0^2 n^2) \quad (n = 1, 2, 3, \text{ etc.})$$

R_H being Rydberg's constant, K_0 the square of the refractive index and m^*/m the quotient of the effective mass to the rest-mass of the electron. By assuming this quotient is near to unity, approximate values for the "optical" spacing can be calculated from the refractive index. According to the value of K_0 , thermal dissociation of an exciton to yield a positive hole and an electron in the conduction band may be easy or difficult.

Optical absorption spectra measured at low temperatures⁵²⁻⁵⁴ afford the best route to exciton levels [see section 6(b)]; results of this sort have been obtained for the azides of Na, K, Rb, Cs, Tl, and Ag.

A third route is open when measurements of the activation energy, E , of photoconductivity have been made [see section 6(c)]. This activation energy is related to the optical energy of the exciton level by the expression $E = (K_0/K_s)\epsilon^{\text{opt.}}$. The quotient (K_0/K_s) of the optical and static dielectric constants arises from the difference between the "instantaneous" nature of an optical process (Franck Condon principle) and the opportunities for rearrangement in a thermal process.

(iii) *The height of the exciton levels above the full (valence) band.* The long wavelength "edge" of the optical absorption spectrum is commonly accepted⁴⁷ as the measure of the energy needed to raise electrons from the full band to the exciton levels. As the temperature is lowered, all the spectral features become clearer. By careful experimentation it is possible to identify, within the absorption "edge", absorption maxima which correspond to transitions to particular exciton levels, and thus to infer the spacing of the exciton levels as well as their distance from the full band.

(iv) *The energy gap between the full band and the conduction band.* This gap (see Fig. 4) is the sum of two of the energies $h\nu$ and R_H/K_0^2 whose determination has been described. It is also independently measurable under favourable circumstances, since it is the energy required to induce intrinsic photoconductivity (unaided by thermal dissociation of excitons). Selection rules forbid the transition from the top of the full band to the bottom of the conduction band; neighbouring transitions can, however, be observed.

(v) *The depth of the conduction band.* The energy Ψ required to liberate completely an electron from the bottom of the conduction band is arrived

⁵² Deb, *J. Chem. Phys.*, 1961, **35**, 2122.

⁵³ Deb and Yoffe, *Proc. Roy. Soc.*, 1960, *A*, **256**, 514.

⁵⁴ McLaren and Rogers, *Proc. Roy. Soc.*, 1957, *A*, **240**, 484.

at for the azides by a combination^{47,55} of theoretically calculated and experimentally measured properties. In the symbols normally⁴⁷ used:

$$N h\nu + R_H/K_0^2 + \frac{1}{2}Ne\Phi + N\Psi = W_L + E$$

The significance of the first two terms on the left is clear from Fig. 3. The terms on the right are $W_L (= U)$, the lattice energy, and E , the electron affinity, of the azide ion. In the term $\frac{1}{2}Ne\Phi$, Φ is the electrostatic potential at the vacant lattice point, *i.e.*, a site from which N_3^- has been removed; it arises from the induced dipoles of the surrounding ions. Experimental values may exist for $Nh\nu$, for E , and for R_H/K_0^2 ; calculated values consistent with experiment exist for W_L ; calculated values must be derived for Φ (an account is given⁵¹ by Mott and Gurney). In this way, values are obtained for Ψ . When the necessary experimental data are not available, a reasonable approximation of Ψ may be guessed from known values of Ψ for the corresponding bromides.

(vi) *Electron traps.* The energy levels discussed above are those appropriate to an ideal, infinite lattice. Real crystals are not infinite and even if pure would have imperfections; in practice they are never absolutely pure and foreign atoms are also present. Thus, there are additional energy levels for electrons and, correspondingly, additional sites in the lattice where electrons may be trapped to form entities of varying stability. They are considered further in Sections 6(d) and 6(e).

(b) Optical Absorption Spectra in the Visible and Ultraviolet Regions.—

The data necessary for the construction of energy-level diagrams, such as those of Fig. 4, come principally from measurements on absorption spectra in the visible and near ultraviolet regions. Azides resemble halides and the (reasonably complete) studies of the alkali-metal and silver halides have been of great value in interpreting the corresponding experimental data for azides.

The earlier workers (beginning with the work on KN_3 by Garner and Maggs⁵⁶ in 1939), who made measurements at room temperature, observed an even simpler form of absorption spectrum than that shown in Fig. 5a, reporting a featureless sigmoid curve, rising sharply in intensity (at around 2000 Å for alkali-metal azides and around 3500 Å for heavy-metal azides) to values for ϵ of *ca.* $10^5 \text{ cm}^2 \text{ mole}^{-1}$. These absorptions correspond to transitions from (the most densely populated part of) the valence bands to the conduction bands. Absorption spectra of this sort have been recorded² for sodium,⁴⁹ potassium,⁵⁷ and barium⁴⁹ azides and for thallium(I)⁵⁷ silver,⁵⁴ copper(I),⁵⁷ mercury(I),⁵⁸ and lead⁵⁹ azides. The energy diagram (Fig. 3) suggests that the onset of this continuum should be preceded by a

⁵⁵ Gray and Waddington, *Proc. Roy. Soc.*, 1957, *A*, **241**, 110.

⁵⁶ Garner and Maggs, *Proc. Roy. Soc.*, 1939, *A*, **172**, 299.

⁵⁷ Evans and Yoffe, *Proc. Roy. Soc.*, 1959, *A*, **250**, 346.

⁵⁸ Deb, Evans, and Yoffe, *Nature*, 1957, **180**, 294.

⁵⁹ McLaren, Ph.D. Dissertation, Cambridge, 1957.

set of sharp lines corresponding to transitions to discrete exciton levels; these are seen only when disturbances from lattice vibrations are reduced by lowering the temperature. Proceeding in this way, McLaren and Rogers⁵⁴ first observed the separate absorption peak corresponding to transitions to the exciton levels in silver azide; subsequently, Deb and Yoffe⁵⁵ resolved two exciton levels in both silver azide and thallos azide. Recently Deb⁵² has reported the exciton spectra of sodium, potassium,

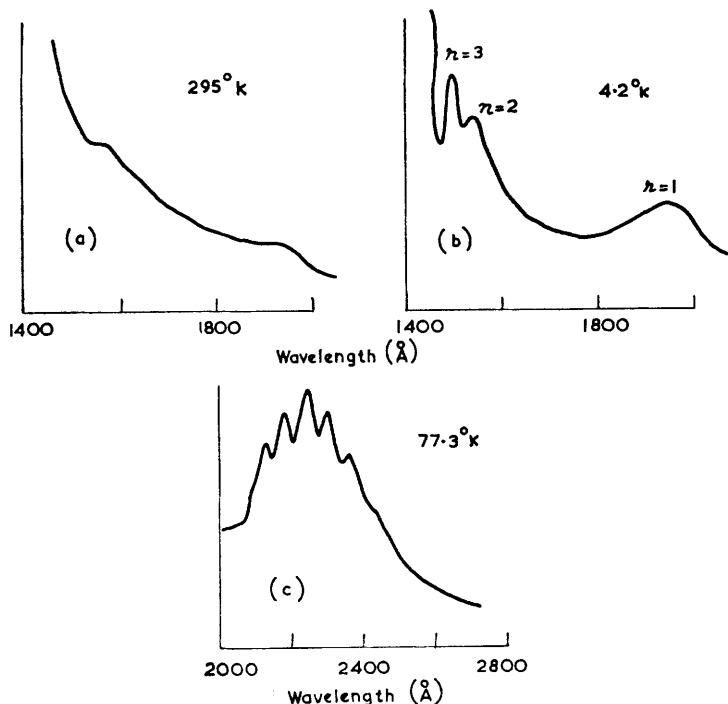


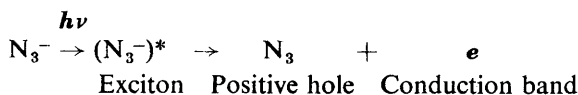
FIG. 5. Principal features of the absorption spectra of an alkali-metal azide (CsN_3). (a) The structureless absorption at room temperature, (b) development of structure (exciton bands) at liquid-helium temperatures, and (c) the evidence for a low-lying excited state of the azide ion.

rubidium, and caesium azides. In Fig. 5(b) is illustrated diagrammatically the exciton spectrum of caesium azide at 4°K . In addition to the exciton levels, a low-lying electronic state corresponding to absorption of ultraviolet radiation with $\lambda = 2225 \text{ \AA}$ has been discovered by Deb; that spectrum (showing vibrational structure) is displayed in Fig. 5(c).

(c) **Photoconductivity.**—When light of a wavelength just shorter than that of the absorption edge falls on thallos azide,^{57,60} silver azide⁵⁴ or

⁶⁰ Evans and Yoffe, *Nature*, 1959, **183**, 4670; Camp, Deb, Evans, Montague-Pollock, and Yoffe, in "Reactivity of Solids," ed. J. H. de Boer, Elsevier, Amsterdam, 1960, p. 321.

potassium azide⁴⁹ (at room temperature) the first two show enhanced electrical conductivity while the third does not. Such photoconduction is temperature-dependent, falling as the temperature is reduced. It arises from the thermal dissociation of optically formed excitons to yield positive holes and electrons in the conduction band:



The difference between the two types of behaviour reflects the different energies necessary to dissociate the excitons of KN_3 on the one hand and of the heavy metal azides on the other. The activation energy for photoconductivity, determined from the slope of a graph of $\log(\text{conductivity})$ against $1/T$ ($^\circ\text{K}$), is the energy required to dissociate an exciton thermally, and it is thus possible and of interest to compare this observed activation energy for photoconduction with that predicted from (a) optically observed exciton levels, and (b) theoretically calculated energies of exciton dissociation. The figures are as follows:

Thermal energy of activation of photoconductivity (kcal. mole⁻¹)

| | From temp. coefficient of photo- conductivity | From optical absorption spectra | Calc. from $R_H/K_0^2n^2$ |
|---------------|---|---------------------------------------|------------------------------|
| Thallos azide | 7.5 | 6.9, 7.5 | |
| Silver azide | 8.8 | 7.5 | 7.5 |

All these azides show intrinsic photoconductivity when the irradiating wavelength is sufficiently short for electrons to be promoted directly into the conduction band.

(d) **Colour Centres.**—It is not unexpected that colour centres (*i.e.*, new optical absorption bands), resembling the well known bands (F , V , etc.) of the alkali-metal halides, should develop in the azides on exposure to ultraviolet light or X -rays, although it is found that the resemblances appear only when both irradiation and observation are carried out at low temperatures. It is convenient to separate this discussion of more or less reversible optical changes from the discussion of permanent photolysis considered in Section 7. As the azide literature is somewhat conflicting (especially in detail) and the precise relevance of colour centres* in azides to other phenomena not yet established beyond dispute, only an outline account is given (two recent papers⁶¹ may be consulted for further detail and leading references).

* The whole field of colour centres has been in a state of upheaval⁶⁴ in recent years.

⁶¹ Heal and Pringle, *J. Phys. and Chem. Solids*, 1960, **15**, 261; Cunningham and Tompkins, *Proc. Roy. Soc.*, 1959, *A*, **251**, 27.

So far, although the loss of its charge by an anion (to form a positive hole) has been envisaged, the positional imperfections^{62,63} of the crystal lattice [section 5(d)] have not been taken into account. To understand the development of colour centres (*i.e.*, of new absorption bands) it is necessary to consider a lattice containing such imperfections, and in particular, lattice vacancies,⁶³ *viz.*, unoccupied anion and cation sites. A vacant anion site behaves like a positive charge; it can trap an electron in a potential-well in one of a series of Bohr orbits. Transitions from the lowest to other orbits commonly absorb optical energy corresponding to the visible region, and one electron so trapped at a vacant anion site is called an *F*-centre. A second electron can also be trapped at the same site; this constitutes an *F'* centre. The *V*-centre, once thought to be an electron trapped at a vacant cation site, is an enigma, though *V_K* centres in KCl are known to arise from Cl₂⁻. Other symbols (*R*, *M*, *N*, etc.) have been given⁶¹⁻⁶³ to colour centres involving vacancies in pairs.

F-bands in the visible, *V*-bands in the ultraviolet, and other bands at longer wavelengths, have all been reported^{61,62} in sodium, potassium, rubidium, and caesium azides exposed to *X*-radiation at liquid-nitrogen temperatures. At room temperatures, potassium azide develops two bands in the red ascribed to *R*-centres. Rather similar results are obtained when ultraviolet illumination is used (2537 Å at -196°).

All assignments are derivative, being based on similarities with related observations on the more thoroughly investigated⁶³ alkali halides; it is now known that some of those are wrong in detail; for recent work, see the papers⁶⁴ of Kanzig and of Kingsley.

(e) Species revealed by Electron Spin Resonance Studies.—A powerful new technique for investigating species with unpaired electrons is provided by electron spin resonance measurements. Such work has transformed the knowledge of defects and colour centres in halides, and, though in its infancy, will greatly influence interpretation of azide results. Investigations up to 1962 have been mainly of azides that have been partially decomposed at low temperatures (77°K to room temp.) by ultraviolet light or ionising radiations (*X*-rays, γ -rays, electron bombardment) because these conditions afford the highest concentrations of detectable species.

Since only electron spins are observed, the nuclei present are deduced by inference from fine structure of the spectra. The species so far identified⁶⁵ include N₄⁻, N₂⁻, and N; they do not yet include the \cdot N₃ radical. The entities thought to be N₄⁻ and N₂⁻ are produced by ultraviolet or γ -radiation; nitrogen atoms are produced only by γ -radiation and are short-

⁶² Rees, "Chemistry of the Defect Solid State," Methuen, London, 1954; Garner, "Chemistry of the Solid State," Butterworths, London, 1955.

⁶³ Seitz, *Rev. Mod. Phys.*, 1946, **18**, 384; 1954, **26**, 7.

⁶⁴ Kanzig, *J. Phys. and Chem. Solids*, 1958, **9**, 70; Kingsley, *Phys. Rev.*, 1961, **122**, 722.

⁶⁵ King *et al.*, *J. Chem. Phys.*, 1960, **32**, 940; **33**, 1266; 1961, **34**, 1499; **35**, 1422; Shuskus, Young, Gilliam and Levy, *J. Chem. Phys.*, 1960, **33**, 622; *Phys. Rev.*, 1962, **125**, 451; Horst, Anderson, and Milligan, *J. Phys. and Chem. Solids*, 1962, **23**, 157.

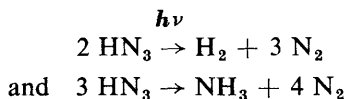
lived above *ca.* -170° . It is to be presumed that these entities are important in radiation damage; their contributions, if any, to thermal and photochemical decomposition are unknown.

7. Isothermal Decomposition of the Azides

The slow decomposition of azides may be brought about in a variety of ways, of which the most important are exposure to heat or light. Nitrogen is always produced but, as is to be expected, pathways and end-products differ for covalent and ionic azides, although, within either family, there are many resemblances between photochemical and thermal decompositions. The sub-divisions below recognise this fact, though non-metallic azides are dealt with very briefly to display their main characteristics for comparison and contrast with the salts. It is convenient to defer consideration of self-heating (although decomposition is almost always exothermic) until Section 8, where self-supporting reaction is discussed.

(a) Thermal and Photochemical Decomposition of the Non-metallic Azides.—The weakest bond in the covalent azides is the link $\text{RN}-\text{N}_2$; this is still so even if dissociation has to be to an excited state [as is demanded by theory; see Section 4(c)(ii)], and all the experimental results suggest that it is this bond which breaks in the initial step of both thermal and photochemical decomposition. Accordingly, the observed stoichiometry is to be explained in terms of the reactions of RN biradicals ("nitrenes"); such explanations are to be found in standard texts.⁶⁶ When $\text{RN} <$ dimerizes, the azo-compound $\text{RN}:\text{NR}$ results; this product is formed in the thermal decomposition of phenyl azide. Alternative subsequent steps include rearrangement (as is found, *e.g.*, in the thermal and photochemical decomposition⁶⁸ of Ph_3CN_3 , trityl azide) and insertion reactions. In the latter, RN ends between two previously linked atoms (*e.g.*, $\text{C}-\text{H}$ or $\text{C}-\text{C}$), a reaction step which has been brilliantly exploited⁶⁹ in a recent synthesis of the alkaloid, conessine.

Hydrogen azide decomposition is stoichiometrically constrained to lie between the two extremes:



Photolysis^{25,26} yields nitrogen and ammonium azide (from $\text{NH}_3 + \text{HN}_3$); complete thermal decomposition (if carried out at temperatures too high

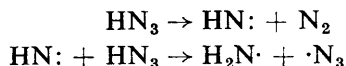
⁶⁶ Sidgwick, "Organic Chemistry of Nitrogen," ed. Taylor and Baker, 3rd edn., Oxford Univ. Press, London, 1942; Moeller, "Inorganic Chemistry," Wiley, New York, 1952; Yost and Russell, "Systematic Inorganic Chemistry," Prentice Hall, New York, 1946. For more recent work see papers cited in ref. 69.

⁶⁷ Russell, *J. Amer. Chem. Soc.*, 1955, **77**, 3487.

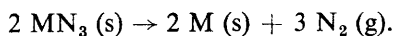
⁶⁸ Deb and Yoffe, *Proc. Roy. Soc., A*, **256**, 528; Saunders and Ware, *J. Amer. Chem. Soc.*, 1958, **80**, 3328.

⁶⁹ Barton and Morgan, *J.*, 1962, 622.

for ammonium azide to be stable) yields nitrogen, hydrogen, and ammonia; it appears^{25,26} to be mainly heterogeneous until rather high (*ca.* 800°) temperatures are reached. There is no clear evidence otherwise for the direct primary photolytic production of N₃ radicals, and the azide radicals observed⁷ in flash photolysis are thought to be secondary reaction products arising, *e.g.*, from the reactions:

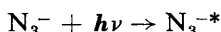


(b) Thermal and Photochemical Decomposition of the Metallic Azides.—Thermal and photochemical decomposition of the metallic azides results in the formation* of metal and nitrogen



The simplest way to follow decomposition is thus to follow the evolution of nitrogen, and practically all kinetic data (velocity constants, activation energies, etc.) have been so obtained. In general, decomposition cannot be described by simple laws (and there is not unanimity† on which particular expressions should be used to represent all or part of the pressure–time curves). Evans, Yoffe, and Gray² give a tabular summary of most results reported before 1960. Moreover, pressure measurements reveal nothing about the collapse of the solid azide lattice during decomposition to the metal, although separate visual studies have been made of nucleus formation, and it has been found that decomposition can proceed with a lower activation energy at the metal–metal azide interface. Establishment of the detailed mechanism is thus remote. However, the main outlines are discernible for silver^{50,54,71} and thallous^{53,68,72} azides and for potassium^{49,73,74} and barium⁷⁵ azides, and these examples are discussed below. In each, the key step is removal of the electron from the azide ion to yield the azide radical.

(i) *Thallous and silver azides.* In both these cases, the initial step in photochemical decomposition is exciton formation:



The next step is decomposition of the exciton, *i.e.*, thermal loss of the

* In some cases⁷⁰ (*e.g.*, CaN₃) the nitride is also formed, but this seems to occur only as a subsequent reaction between the nitrogen and the metal.

† It is characteristic of the state of the subject that the careful re-examination of any system reveals features which were unnoticed though significant. For a recent example, see the work of Sheppard *et al.*⁷⁴ on photolysis.

⁷⁰ Garner and Reeves, *Trans. Faraday Soc.*, 1955, **51**, 694; Tompkins and Young, *Discuss. Faraday Soc.*, 1957, No. 23.

⁷¹ Bartlett, Tompkins, and Young, *Proc. Roy. Soc.*, 1958, *A*, **246**, 206.

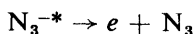
⁷² Gray and Waddington, *Chem. and Ind.*, 1955, 1555.

⁷³ Jacobs and Tompkins, *Proc. Roy. Soc.*, 1952, *A*, **215**, 265.

⁷⁴ Jacobs and Sheppard, in press; Sheppard, Ph.D. Dissertation, London, 1962.

⁷⁵ Jacobs, Tompkins and Young, *Discuss. Faraday Soc.*, 1959, No. 28, 234.

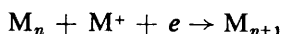
electron to the conduction band, leaving a positive hole (azide radical)



Nitrogen gas is formed by the reaction of two azide radicals at the surface; any azide radicals formed internally can appear at the surface by an electron-transfer mechanism:

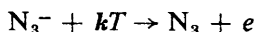


Metal is formed by the mechanism (suggested⁵¹ by Mitchell)



There is at present no good experimental evidence that silver is formed *internally* in a crystal (*e.g.*, along dislocations). For the photochemical decomposition^{50,54} of silver azide (orthorhombic, low-temperature form) and thallos azide^{53,68} the experimental values of the activation energies are in reasonable accord with the thermal energy required to dissociate the exciton, and that step is thought to be rate-determining.

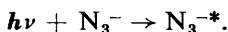
In thermal decomposition, the electron is raised thermally to the conduction band,



but otherwise the mechanism is the same. Experimentally measured⁷¹ activation energies are in approximate accord⁶⁸ with the thermal energies of promotion derived from studies of the physical properties of the azides.

(ii) *Potassium and barium azides.* For these azides a different, though related, mechanism is invoked.

In photolysis it has been suggested^{49,75,76} that an exciton is directly formed,



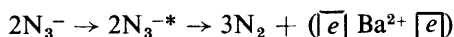
This exciton does not immediately lose its electron to the conduction band; instead, it is trapped at a vacant cation site. At the surface, such trapped excitons may decompose in pairs to form nitrogen. The electron is lost to form an *F*-centre and the activation energy of photochemical decomposition represents the (small) thermal energy of *F*-centre-formation from excitons. More recently, low-lying excited states of the azide ion have been invoked^{74,77} instead of excitons. It has also been found⁷⁷ for barium azide that there are concurrent processes; one of these is associated with the formation of barium in the crystal matrix and may involve the transfer of electrons from these excited azide ions to small specks of barium—a process with an activation energy between 10 and 20 kcal. mole⁻¹.

In thermal decomposition^{73,74,77} the rate-determining step is thought to be thermal formation of the excited azide ion. The subsequent reaction

⁷⁶ Kanzig, *J. Phys. and Chem. Solids*, 1958, **9**, 70.

⁷⁷ Jacobs, Tompkins, and Pai Verneker, *J. Phys. Chem.*, 1962, **66**, 113.

of the excited ions on adjacent sites leads to molecular nitrogen and metallic barium:



The experimentally observed activation energy of thermal decomposition is to be identified with the thermal energy of formation of the excited species and the 74 kcal. activation energy of nucleus formation with the energy needed to give two such species on adjacent sites.

(c) The Principles underlying Interpretation of Isothermal Decomposition.—In the covalent azides, the structural unit is the individual molecule; the act of decomposition is molecular and does not much depend on the state of aggregation. All the observations^{26,65,69} point to the production of $\text{RN}<$; there is no evidence for the direct formation of the azide radical ($\cdot\text{N}_3$).

In the metallic azides there are no discrete molecules and the structural unit is the anion. Not only is the state of aggregation of great importance but decomposition is sensitive to minor variations such as crystalline form, method of preparation, extent of ageing, etc. For (neutral) nitrogen molecules to be formed from (negative) azide ions the latter must lose their charge. The different ways in which the loss of the electron may occur are the chief origin of differences between different ionic azides, and the electron-energy diagram (Fig. 4) the most effective means of displaying them. Thus, the electron may enter the conduction band—and it can do this either directly, leaving a positive hole (azide radical), or indirectly, after an intermediate promotion to an immobile excited state or to an exciton level. Alternatively, the electron may be trapped either at an intrinsic lattice defect (*e.g.*, at a vacant anion-site, forming an *F*-centre) or at an impurity centre. The role of point defects is becoming increasingly understood; most discussions (see, *e.g.*, refs. 49, 50, 52—55, 57, 58, 60, 61, 68, 70—75) are conducted in terms of them. For instance, the facts (see Fig. 4) that (i) the energy required to form an exciton diminishes in the order KN_3 , TiN_3 , AgN_3 , CuN_3 , while (ii) the energy to dissociate an exciton is much less for TiN_3 or AgN_3 than it is for KN_3 , have been recognised as the basis for observed correlations between azide stability and ionisation potential. It must be recognised that in many ways interpretation of reaction kinetics is still rudimentary. For instance, the influence of electron traps (especially impurity centres) is demonstrable, and this means not only that the reaction mechanism is complex (which is generally acknowledged) but also that the idea of a “rate-controlling step” is likely to be an over simplification. Successful application of the stationary-state hypothesis to assumed kinetic schemes should increase the flexibility of interpretation beyond systems in which one step exclusively governs the rate. It is also true at present that the magnitudes of *A*-factors of the Arrhenius expressions are very much less well understood than those of activation energies.

Finally, there are the problems of crystal surfaces and dislocations. Gaseous nitrogen can form only at a surface, and there is evidence for lowered activation energy of decomposition at the metal-metal azide boundary. In sodium azide⁷⁸ decomposed at 275°, where the progress of a (coloured) boundary between the outer part of the crystal and the inner, undecomposed part can be observed, the different rate of reaction at different faces is marked. The role of the surface⁷⁹ is thus growing more discernible: that of dislocations is still obscure.

8. Self-supporting Decomposition: the Explosion and Detonation of Azides

Perhaps the best known property of the azides is their ability to explode and detonate when subjected to shock. Explosion may also be initiated in other ways: these include subjection to heat, light, or electric sparks, to the passage of a current, and to friction. Explosion, once initiated, may take various forms, of which the least destructive is deflagration (burning) and the most destructive detonation.

There have been numerous discussions in the past (for comprehensive references, see Bowden and Yoffe^{80,81}) of factors affecting the "stability" and "sensitivity" of azides, but these are often marred (i) by confusion of definitions, *e.g.*, between the thermodynamic and kinetic senses of the term "stability", (ii) by failure to distinguish between initiation and propagation so far as "sensitiveness" is concerned, and (iii) by the use of quantities such as ignition temperatures which were often ill-defined and sometimes without significance.

The principles underlying the more successful analyses of the initiation and propagation of explosion in azides may be summarised as follows: (1) in solids, self-supporting reaction proceeds by a self-heating mechanism, the energy of decomposition serving to bring about the decomposition of further material. Initiation by heating thus requires no special assumptions, and ideas⁸² of branched chains have not proved helpful; (2) mechanical initiation (impact, friction) operates by way of a localised degradation of energy to heat, and is thus a province of the thermal domain; (3) the properties of isothermal decomposition must be well characterised and adopted as the starting point for any useful analysis to be possible. When these data are lacking, only empirical correlations are possible. Something like this is true of azide burning, since there are no data for isothermal kinetics at high temperatures. For detonation, theory and experiment often fail to overlap, since experiments commonly are done on small quantities of azides, while theory applies to infinite amounts.

(a) Exothermicity of Decomposition.—Azides explode only if reaction is

⁷⁸ Secco, *Canad. J. Chem.*, 1962, **40**, 2191.

⁷⁹ Bowden and Yoffe, *Endeavour*, 1962, **21**, 125.

⁸⁰ Bowden and Yoffe, "Initiation and Growth of Explosion in Liquids and Solids," Cambridge University Press, 1952.

⁸¹ Bowden and Yoffe, "Fast Reaction in Solids," Butterworths, London, 1958.

⁸² Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576.

exothermic, and normally yield gaseous nitrogen and solid metal so that the heat released on explosion equals the standard enthalpy of formation of the salt. If the metal is vaporised, allowance should be made for the latent heat of sublimation. If the metal reacts with nitrogen, or if there is an atmosphere of oxygen in which it can burn, allowance should be made for the additional heat release¹² of nitridation or oxidation.

TABLE 4. *Standard enthalpy of formation, ΔH_f° (kcal. mole⁻¹), of metal azides at 25° (rounded values).*

| Univalent-metal azides | | | | Bivalent-metal azides | | | |
|------------------------|------|--------------------------------|------|-----------------------|-------|--|-------|
| LiN ₃ | 2.6 | NH ₄ N ₃ | 26.8 | CaN ₆ | 11.0 | Hg ₂ N ₆ | 141.5 |
| NaN ₃ | 5.1 | CuN ₃ | 67.2 | SrN ₆ | 1.7 | PbN ₆ (α or β) | 115 |
| KN ₃ | -0.3 | AgN ₃ | 74.2 | BaN ₆ | -5.3 | MnN ₆ | 94 |
| RbN ₃ | -0.1 | TlN ₃ | 55.8 | ZnN ₆ | 50.8 | NiN ₆ .H ₂ O | 31.7 |
| CsN ₃ | -2.4 | | | CdN ₆ | 106.2 | CuN ₆ | 140.4 |

Table 4 lists standard enthalpies of formation¹² of the more important metal azides. The entries in it for manganese and nickel azides require confirmation; other figures are unlikely to be seriously in error.

(b) **Initiation of Explosion by Heating.**—The simplest situation for theory to examine is that presented by a homogeneous mass of explosive which is imagined to have been brought instantaneously to some uniform temperature and is undergoing exothermic decomposition. More complex is the situation where heating is localised, and more complex still that where heating is both localised and transient. However, subject to the limitations of various (physically reasonable) assumptions, thermal-explosion theory⁸³ throws light on all these cases. The mathematical equations are often too difficult for simple analytical solutions, and developments⁸⁴ have been made in two ways. In one, electronic computers have been employed to solve specific problems. In the other, physically reasonable approximations have been employed to reduce the general equations to a solvable form. Since the latter lends itself more readily to a general discussion, it is adopted here, but it must be remembered that developments are occurring along both paths.

(i) *Uniform heating: spontaneous ignition.* An analysis by Semenov showed that, in many instances, quite small (15°) rises in temperature preceded thermal explosion, and that very little reaction occurred during the induction period. Frank-Kamenetskii,⁸³ recognising and exploiting the significance of these results, gave an elegant answer to the question of what determines whether or not explosion occurs. His result may be expressed as follows for a reaction following the Arrhenius law. If δ is

⁸³ Frank-Kamenetskii (transl. N. Thon), "Diffusion and Heat Exchange in Chemical Kinetics," Princeton University Press, 1952.

⁸⁴ Gray and Harper, *Trans. Faraday Soc.*, 1959, **55**, 581; "Reactivity of Solids," ed. de Boer, Elsevier, Amsterdam, 1961; Thomas, *Trans. Faraday Soc.*, 1958, **54**, 60.

written for the group of terms ($2r$ is diameter of reactant, λ its thermal conductivity): $(r^2/\lambda) (E/RT^2) QA \exp(-E/RT) c$, then the explosion criterion may be expressed by the relation:

$$\delta \leq \delta_{cr} \text{ where } \delta_{cr} = 0.88 \text{ (slab); } 2 \text{ (cylinder); } 3.32 \text{ (sphere)}$$

This dimensionless group shows how the physicochemical parameters (A , E , Q , and λ) of the reactant are reflected in the critical conditions (r , T , c) which have to be satisfied for ignition. Most important is temperature, by virtue of its appearance in the exponential. There is, however, no "critical temperature" as such for explosion, the critical value being different for different sizes and concentrations; nevertheless if, e.g., r and c are kept the same, ignition temperatures can have use and significance. There are experimental data⁸⁵ for the influence of size on the explosion temperature for cadmium azide crystals in the form of thin plates. At 320°, crystals having a thickness greater than 24 μ explode, whereas thinner ones decompose slowly without explosion; the critical thickness decreases with increase in temperature. Similar behaviour is reported^{81,85} for silver azide, lead azide, mercurous azide, and cuprous azide.

Sensitisation by impurities. The physical and chemical properties of inorganic solids can often be changed considerably by the introduction of traces of an impurity. Foreign cations and anions and metallic impurities have been found⁸¹ to influence behaviour. Though their action is by no means fully understood, it has been explained² in general terms by invoking the formation of electron traps. This type of interpretation, to be satisfactory, should be able to explain the influence on explosiveness in terms of observable influence on isothermal kinetics, and this is not always the case.

(ii) *Localised and transient heating; hot spots.* If, instead of a general rise of temperature occurring at a rate controlled only by the rate of exothermic reaction, the result of a pulse of thermal energy is considered, the initial conditions are different and the solutions modified. Such transient heating may be uniform, or localised as, e.g., in ignition by a hot wire. A most important special case of thermal initiation is that in which intensely localised thermal energy is released transiently. The question now is, will a self-supporting reaction develop or die away in the region surrounding the "hot spot". Analysis of the situation along the lines followed previously leads to new relations among the same terms. A recent treatment⁸⁶ (from which earlier work may also be traced) is that by Boddington.

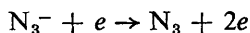
The reason for the importance of this special case is its relevance to almost all instances of mechanical initiation, to spark ignition, and to ignition by a hot wire.

⁸⁵ Bowden and Singh, *Proc. Roy. Soc.*, 1954, *A*, 227, 22.

⁸⁶ Boddington, Ph.D. Dissertation, Cambridge, 1961; "Ninth Symposium (International) on Combustion," Academic Press, 1963, p. 287.

(c) **Initiation of Explosion by Means other than Direct Heating.**—It is convenient to distinguish various other (*e.g.*, electrical, mechanical, and optical) means of ignition. When these are examined more closely, however, certain resemblances are more significant than the differences. First, a thermal element is common to them all; secondly, the heating involved is localised and transient; thirdly, when a self-supporting explosive reaction starts from a localised region, though this may be small, it is not small on a molecular scale; for initiation to occur, many millions of molecules must decompose.

(i) *Electrical initiation.* Electrical ignition may be achieved by passing an electric current through a metallic conductor passing between azide particles (hot wire), by electric sparks, and by dielectric break-down. Hot-wire ignition is clearly thermal, and its course may be evaluated by thermal-explosion theory. To a first approximation, passage of an electric spark is effectively a release, in a very small volume, of a known amount of energy—an instantaneous hot spot—and its effect (or the thermal part) is thus again susceptible to calculation; that this is not the whole story is proved by the different influences of various types of discharge. Dielectric break-down occurs in silver azide when crystals are subjected to an intense electric field. Metallic filaments are not formed and field-emission from the cathode has been proposed as the origin of initiation by dielectric break-down. The electrons which enter the crystal have sufficient energy to induce decomposition by ejecting electrons from azide ions:



(ii) *Optical initiation of explosion.* It is possible to initiate explosion in an azide by exposure to an intense flash of light. Formerly it was thought⁸⁷ that light was wholly degraded to heat, most of the degradation occurring in a very thin (*ca.* 10^{-4} cm.) layer near the surface, and that this thermal energy in turn brought about decomposition. It is now recognised⁵⁷ that optical formation of excitons which dissociate thermally to azide radicals (positive holes) and electrons is important as a primary step. Combination of the positive holes liberates nitrogen exothermically and assists in heating the remaining azide. The sensitising action of dispersed particles of gold is thus explicable in terms of their action as electron-traps, though the precise mode of action is not clear. However, the idea of self-supporting exothermic surface decomposition is common to both views.

(iii) *Mechanical initiation.* When an azide is subjected to impact or friction,^{80,81} the explosion which may result is generally thermal in origin. The mechanical energy is first degraded to heat; small, localised regions of about 10^{-5} — 10^{-3} cm. diameter become intensely hot. Thermal decomposition takes place there, and self-supporting decomposition

⁸⁷ Eggert, *Z. Naturforsch.*, 1953, **86**, 389; *Physik Bl.*, 1954, **10**, 549; Courtney-Pratt and Rogers, *Nature*, 1955, **175**, 631.

spreads. Most commonly, the hot spot is a trapped pocket of air^{80,81} which has been compressed adiabatically during the impact.

Flying fragments⁸¹ may also induce explosion; lead azide used in this way has been shown⁸⁸ to bring about the ignition of both a second particle of lead azide and a crystal of silver azide. Ultrasonic waves and shock waves have proved similarly effective⁸¹ in inducing explosion mechanically.

(iv) *Initiation by α -particles, neutrons, electrons, fission-fragments, or γ -rays.* An azide subjected to the influence of ionising radiations will, in general, undergo decomposition but not explosion.^{80,89} This result, which is consistent with the observations made on ignition by heat, shock, and light, is a consequence of the need to induce the decomposition of a large number of adjacent azide molecules in order to initiate explosion. If the ionising radiation is intense enough, an ignition may be observed which owes its origin to a generalised heating of the crystals. The change of viewpoint away from the idea that the simultaneous disintegration of a small group (or, in an extreme form, a pair) of adjacent molecules is enough to initiate explosion is a significant advance in understanding.

(d) **Burning.**—Since, in flame propagation, one is concerned with very steep temperature and concentration gradients, the problems arising are intrinsically more difficult than those of the pre-explosion period in spontaneous ignition. While theories of laminar flame propagation in gases now account in a relatively satisfactory manner for the experimental observations, the complexities in solid systems are much greater. Also, it is not experimentally easy to approach the infinite plane flame-front of theory, most observations referring to experiments on thin films of powdered azides or on very small single crystals. However, the general conclusion, that the rate of burning is controlled by the interplay of rates of chemical reaction and of the transport of heat and matter, focuses attention on the need for thorough investigations of these aspects. Recent accounts^{90,91} of the ignition of explosive inorganic azides are given by Bowden and Yoffe and their co-workers.

(e) **Detonation.**—Detonation is not only violent and swift, but its onset may also be extremely rapid. High speed photography^{79–81} shows delays as short as 10^{-7} sec. between initiation and the onset of detonation. The common absence of any extended burning region may be correlated with the fact that decomposition of inorganic azides necessarily takes place in few steps so that the energy of decomposition is liberated rapidly. The detonation velocity, D , is the only parameter commonly accessible to measurement; values range from *ca.* 10^5 cm. sec.⁻¹ for very thin (10^{-2} cm.)

⁸⁸ Belya'ev and Khariton, *Acta Physicochim.*, U.R.S.S., 1936, 5, 757; Courtney-Pratt and Rogers, *Nature*, 1955, 175, 176.

⁸⁹ Bowden and Montague-Pollock, *Nature*, 1961, 191, 556.

⁹⁰ Deb, Evans, and Yoffe, "Eighth Symposium (International) on Combustion," Williams and Wilkins, Baltimore, 1962, p. 829.

⁹¹ Bowden, Camp, and Montague-Pollock, "Eighth Symposium (International) on Combustion," Williams and Wilkins, Baltimore, 1962, p. 836.

unconfined "films" of crystals to *ca.* 5×10^5 cm. sec.⁻¹ in stable, high velocity detonation. Deb, Evans, and Yoffe⁹⁰ give values for *D* as follows:

| | | | | | | |
|----------------------------------|------------------|------------------|------------------|------------------|--------------------------------|------------------|
| Azide | TlN ₃ | AgN ₃ | CuN ₃ | PbN ₆ | Hg ₂ N ₆ | HgN ₆ |
| <i>D</i> (m.sec. ⁻¹) | 1480 | 2170 | 2720 | 2300 | 2350 | <i>ca.</i> 3000 |

As is expected of this "hydrodynamic" phenomenon, detonation does not show marked dependence (such as is shown, *e.g.*, by deflagration) on the structure of the azide in the solid state. The speed and scale of the phenomenon (reaction times less than a microsecond and reaction zones thinner than a millimetre, corresponding to the traversal of molecular dimensions in the time of a single molecular vibration) together with the incidence of intense ionisation have so far prevented the discernment of details of processes in the reaction zone itself.

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